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Polyalkylene Glycols

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I. INTRODUCTION

Polyalkylene glycols are unique among synthetic lubricants because of their high oxygen content. As lubricants, they are exceptionally clean, allowing use where petroleum products would build tars and sludges. By varying their structure, one can vary their solubilities from water soluble to water insoluble. They are the only lubricants available with water solubility. A product of World War II, they quickly found uses where petroleum-based lubricants fail. This chapter covers lubrication uses only; however, polyalkylene glycols have many applications in addition to lubrication.

II. HISTORICAL DEVELOPMENT

Polyalkylene glycols are one of many important industrial chemicals developed during World War II. This work was performed by H. R. Fife, and to a lesser extent by R. F. Holden, as a joint development project between Union Carbide Chemicals and Plastics Company Inc. (then known as the Union Carbide and Carbon Corporation) and the Mellon Institute of Industrial Research in Pittsburgh. Union Carbide Chemicals and Plastics Company Inc. held the original patents for the common lubricants [1–3].

The first use of polyalkylene glycols was in water-based hydraulic fluids [4]. First developed for the navy [5] for use in military aircraft, these compounds were being investigated as early as 1943. They were formulated from water, ethylene glycol, a polyalkylene glycol that acted as a thickener, and an additive package. In military aircraft, it is important that fires not break out when bullets or shrapnel sever hydraulic lines. The final test the Navy conducted was to fire a 50-caliber incendiary bullet, shredded by first passing through a steel baffle, through 1-gallon cans of test fluid. This test was passed by UCON Hydrolube U [6] using a polyalkylene glycol thickener.

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More severe flammability requirements were established after the war. Hydraulic fluids to be used for missile ground handling equipment were developed that would not burn in a 100% gaseous oxygen atmosphere when the fluid was ejected at a pressure of 3000 psi in the presence of a continuous electric discharge ignition source [7]. Aqueous solutions of polyalkylene glycols could be formulated to pass this test.

When polyalkylene glycols were first developed, the high viscosity indices and low pour points were quickly identified [8], leading to the use of these compounds in all-weather, heavy-duty brake fluids. Besides being fluid at temperatures that would cause petroleum products to freeze, they were also water tolerant. Small amounts of water contaminants would dissolve, not significantly changing the physical properties of the fluid nor crystallizing at low temperatures. This is still a major use of polyalkylene glycols today.

Polyalkylene glycols were extensively used as aircraft engine lubricants in cold climates [9]. Over 150,000 flying hours were accumulated, mostly in Alaska, using an inhibited polypropylene glycol monobutyl ether. The low pour point allowed aircraft engines to start at temperatures as low as −30°F without diluting the lubricant with fuel, a step that can be used to reduce lubricant viscosity. It was possible to hydraulically feather the propellers using the polyalkylene glycol based lubricant down to −60°F. Clean burn-off, an intrinsic property of polyalkylene glycols, resulted in low levels of carbon deposits and sludge, making engine cleanup easier during maintenance. Polyalkylene glycols were finally judged unsuitable for aircraft engine oils because of factors: corrosion and deposits. Corrosion, due to the tendency of polyalkylene glycols to absorb water, was principally a problem for engine parts exposed to moist air. Corrosion protection additives were not available at that time for polyalkylene glycols. The hard deposits consist primarily of lead from the fuel. The clean burn-off tendency of the fluid apparently was responsible for this. The lead deposits formed with petroleum as an engine lubricant are soft and have a lower lead content. It is believed that these unusual lead deposits resulted in valve sticking after about 300–400 hours of operation [10] although no valve sticking was observed if valve clearances were adequate.

Lubrication engineers quickly developed new uses of polyalkylene glycols. The uses developed were for petroleum oil replacement in operations where petroleum oil was not entirely satisfactory and the higher cost of the polyalkylene glycol could be justified. The desirable properties of the polyalkylene glycols include a low tendency to form carbon and sludge, clean burn-off, solvency, high viscosity indices, tolerance for rubber and other elastomers, low pour points, and low flammability.

Polypropylene glycol monobutyl ethers were tested extensively as lubricants for automobile engines [11]. The fluids showed the expected low carbon and low sludge, as well as clean engine parts and satisfactory cranking at low temperature. Over 2 million miles of operation using these oil were experienced. This market was never developed.

Because polyalkylene glycols burn off cleanly, they are desirable to use in high temperature applications where petroleum lubricants would form sludge. They have been used in glass factories to lubricate the turrets of hot cut flare machines or to lubricate the bearings of rollers that smooth glass sheets. When mixed with graphite, polyalkylene glycols are very effective at lubricating bearings of carts being rolled into kilns. After the polyalkylene glycol has burned off, a soft, lubricating layer of graphite is left behind.

Polyalkylene glycols were found to have little or no solvent or swelling effects on most synthetic or natural rubbers. This gave rise to many uses calling for the lubrication of rubber parts, such as rubber shackles, joints, or O-rings, or in the manufacture of rubber parts, where demolding lubricants were needed.

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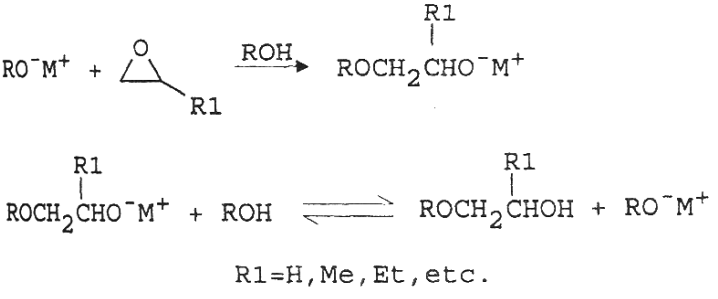
III. CHEMISTRY

A. Nomenclature

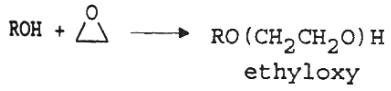
Polyalkylene glycol is the common name for the homopolymers of ethylene oxide, propylene oxide, or butylene oxide; or the copolymers of ethylene oxide, propylene oxide, and/or butylene oxide. Although polyalkylene glycol is the common usage, *Chemical Abstracts* refers to these materials as polyoxyalkylene glycols. The ethylene oxide polymers are generally called poly (ethylene glycols) or poly (ethylene oxides). The *Chemical Abstracts* nomenclature is oxirane polymer. The propylene oxide polymers are known as poly (propylene glycols) or poly (propylene oxides) with a *Chemical Abstracts* name of oxirane, methyl polymer. The butylene oxide polymers are known as poly (butylene oxides) with a *Chemical Abstracts* name of oxirane, ethyl polymer. The copolymers are known as "oxirane, polymer with methyloxirane" or "oxirane, methyl polymer with oxirane," depending on which oxide was used in the greater amount. Butylene oxide polymers are treated similarly. The *Chemical Abstracts* nomenclature does not distinguish between random and blocked copolymers (see below). The individual polymers and the copolymers all fall into the class of polyalkylene glycols. This latter name leads to the acronym PAGs. The acronym PAO has occasionally been used to indicate poly (alkylene oxide), but PAO is commonly used to designate poly (α-olefin).

B. Mechanism of Polymerization

Polyalkylene glycols are prepared by polymerizing epoxides with a starter that consists of an alcohol and a smaller amount of its metal alkoxide, usually the potassium or sodium salt. The epoxide reacts with the metal alkoxide form of one of the starter alcohol molecules to give an alkoxide derivative of a new alcohol. This new metal alkoxide is in equilibrium with all the alcohols present, so that the next reaction of an epoxide can occur either with the molecule that has already reacted or with a different alcohol:



If the epoxide is ethylene oxide, an ethyloxy group results:



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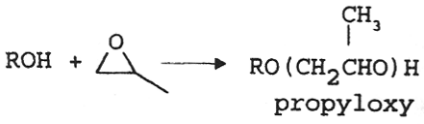
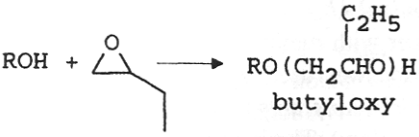
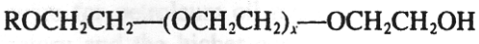
If the epoxide is propylene oxide, a propyloxy group results:



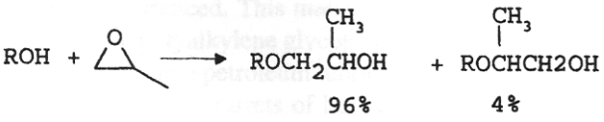
If the epoxide is butylene oxide, a butyloxy group results:



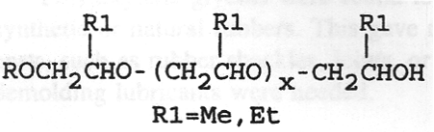
The equilibrium between alcohol and alkoxide determines the molecular weight distribution of the product. The epoxide monomers react with the metal salts of the alcohol at much faster rates than are observed with the alcohols. Whichever alcohol is most acidic will tend to form the alkoxide salts and will be the most reactive toward the epoxide. Once each starter alcohol has reacted with at least one epoxide, all molecules in the system will have approximately the same reactivity. Unless the parent alcohol is extremely unreactive, the fast exchange of metal salt between the growing polymer chains then results in what is nearly a Poisson distribution for molecular weight. The starter alcohols in commercial polymers use relatively reactive alcohols. The Poisson distribution is a much narrower distribution than the most probable or Gaussian distribution. In many applications the narrow distribution is critical, since it means that there is no significant fraction of low molecular weight, volatile, or low-boiling components. In addition, a narrow molecular weight distribution leads to a high viscosity index. Polymerization of ethylene oxide produces a structure like the following:



Ethylene oxide has two reactive sites, and the product is the same no matter which one reacts. The situation is different with propylene oxide and butylene oxide. In this case the ring opening occurs predominantly to produce a secondary hydroxyl group. This result is due to steric factors; the methylene ring position is less hindered than the methylene. For propylene oxide, 96% of the end groups are secondary hydroxyls and 4% are primary hydroxyls:



This leads to a polymer structure approximated as follows:



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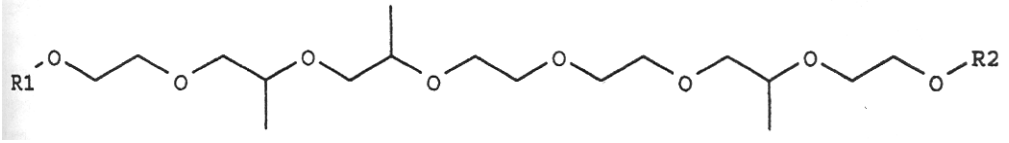
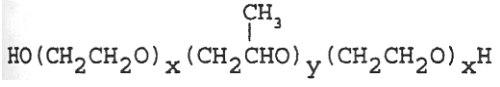
Copolymers of ethylene oxide and propylene oxide have two types of structure, random and blocked. In the random polymer, the two epoxides are co-fed to the starter and will both be incorporated throughout the polymer. They react to give a product that is itself reactive and is in the acid–base equilibrium with all the other alcohols and metal alkoxylates present. To a first approximation, the epoxides are incorporated in a random manner dependent on the relative amounts of each epoxide present and the molecular weight distribution is still approximated by the Poisson model. Polymers with this structure are identified as random copolymers. A portion of the structure of a random ethylene oxide–propylene oxide copolymer is shown schematically:



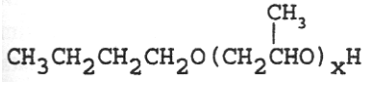
In the block copolymer, an alternative structure is produced by reacting the starter first with one of the epoxides to produce a homopolymer. This can then be reacted with a different epoxide to produce a block copolymer. This name arises from the presence of a chain of one structure connected to a chain with a different structure. A block copolymer produced by feeding propylene oxide to propylene glycol followed by feeding ethylene oxide is shown schematically as follows:



$$HO(CH_2CH_2O)_x(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_y(CH_2CH_2O)_xH$$

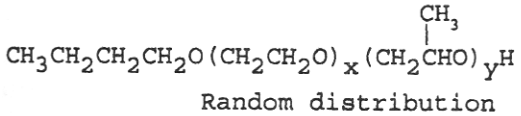
The polyalkylene glycols that are used commercially as lubricants are of five main types.

1. Homopolymers of propylene oxide (polypropylene glycols), which are the water-insoluble type. These show limited solubility in oil. These are typically monobutyl ethers:



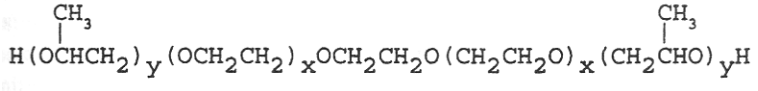
$$CH_3CH_2CH_2CH_2O(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_xH$$

2. Copolymers of ethylene oxide and propylene oxide, which are the water-soluble type. These are typically diols or monobutyl ethers:



$$CH_3CH_2CH_2CH_2O(CH_2CH_2O)_x(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_yH$$

Random distribution



$$H(O\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2)_y(OCH_2CH_2)_xOCH_2CH_2O(CH_2CH_2O)_x(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_yH$$

Random distribution

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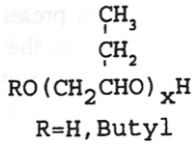
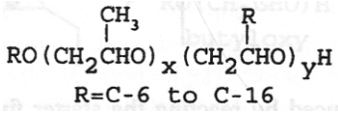
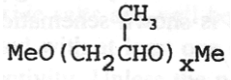
3. Polymers of butylene oxide. These show greater oil solubility than the homopolymers of propylene oxide. They have the following structure:



4. Polymers of propylene oxide and higher epoxides designed to give greater oil solubility. These have the following structure:



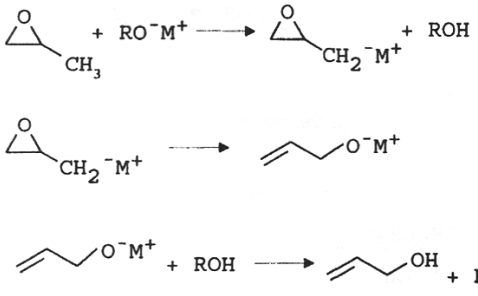
5. Polymers of propylene oxide that are dimethyl ethers:



Polymers consisting of all ethyloxy groups, the polyethylene glycols, are not often used as lubricants, since they tend to crystallize at room temperature when their molecular weight exceeds 600. Nevertheless, solid polyethylene glycols are used in specialty lubrication applications where the solid formulation is advantageous.

The tendency of polyethylene glycol chains to crystallize affects the block polyalkylene glycols. If the blocks of ethyloxy groups are long enough in a block copolymer, pastes or waxes result. Block structures also tend to give the polymers surfactant properties in water. As a result, block polyalkylene glycols are often used as surfactants. However, surfactant-like properties are of little use for most lubrication applications.

The epoxide polymers formed by base-catalyzed reactions typically have molecular weights of less than 20,000. Traces of water in the monomer feed and minor side reactions limit the average molecular weight that can be achieved. The major side reaction for the base-catalyzed polymerization of propylene oxide is the rearrangement of propylene oxide to allyl alcohol. This was recognized as early as 1956 [12]. The rearrangement involves deprotonation of the methyl group on the propylene oxide, followed by intramolecular ring opening:



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This mechanism is supported by kinetic studies with 1, 2-epoxypropane-3,3,3-D, which show a large positive isotope effect [13]. The allyl alcohol formed reacts with ethylene oxide and propylene oxide to yield new polyalkylene glycol molecules, which are monoallyl ethers. This chain transfer reaction limits the ultimate molecular weight that can be achieved with base catalysis. Although rearrangement of butylene oxide is not reported, this compound undoubtedly undergoes a similar base-catalyzed rearrangement. Strong base catalysts that give reduced amounts of unsaturation are reported to be barium and strontium hydroxides [14].

An alternative technology for polymerization can produce much higher molecular weight ethylene oxide polymers. Using coordinate-initiated polymerization, it is possible to produce ethylene oxide polymers with molecular weights in excess of a million. These compounds are produced commercially by Union Carbide Chemicals and Plastics Corporation under the trade name of Polyox. A calcium amide alkoxide suspended in a solvent that does not dissolve the polymer product is used. Ethylene oxide is added and the polymer, not being soluble in the medium, is produced as a granular solid. Polymerization is thought to take place by coordination of the epoxide to an electrophilic site on the catalysts. This coordination activates the epoxide for reaction with the growing chain.

C. Synthesis of Polyalkylene Glycols

Ethylene oxide is a toxic material with a time-weighted average for 8 hours of exposure of 1 ppm and a short-term permissible limit of 5 ppm in a 15-minute period, as determined by the federal Office of Occupational Safety and Health (OSHA). It is highly flammable and has a wide flammable range in air of 3.0–100%. It can explosively decompose if exposed to an ignition source. The flammability is only heightened by a boiling point of 10.4°C, making it a gas at ordinary temperatures. It can be polymerized with acidic, basic, and coordination catalysts, a polymerization that is very exothermic. A very careful study of tile hazards and procedures for safely handling ethylene oxide must be undertaken before the use of this substance is attempted. Similar hazards exists with propylene oxide and butylene oxide.

In the laboratory, it is possible to use glass equipment at atmospheric pressure to prepare ethylene oxide, propylene oxide, and mixed ethylene oxide–propylene oxide polymers. A nitrogen-flushed flask is charged with the starter solution and fitted with a dry-ice condenser. A small amount of the epoxide is fed to the heated flask (typically 100°C or more) and allowed to reflux from the dry-ice condenser. The epoxide charge will be slowly consumed by the polymerization reaction, and the reflux rate will decrease. More epoxide is added at a rate sufficient to keep the system at reflux [15]. The rate can be increased by keeping the apparatus under a slight pressure from a dip tube immersed in an inert liquid. The higher pressure increases the concentration of monomer in the reaction solution. To make a random copolymer, the two oxides are co-fed; a block copolymer requires sequential feeds of the two different epoxides. A similar system can be designed for coordinate-initiated polymerization.

The use of an autoclave for the polymerization will result in much faster rates, since operation at higher pressures is possible, resulting in much higher liquid phase concentrations of the monomers. The epoxide can be fed either by forcing it into the autoclave from a pressurized feed vessel with nitrogen pressure or by pumping it into the reactor. The reactor needs to be equipped with a cooling system and a control scheme to follow and regulate both pressure and temperature. The reactor is heated to the desired operating temperature and the epoxide fed until the pressure has reached the desired level. As the reaction progresses, the pressure will fall and more epoxide can be fed. Pure ethylene oxide vapor can explosively decompose upon exposure to an ignition source. A sufficient amount of nitrogen present before the initiation of the epoxide feed will ensure that the vapor phase does not reach the flammable limit at any time during the

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run. It is critical to keep the inventory of unreacted oxide in the reactor at a level such that the heat of polymerization (20 kcal/mol) can be removed by the cooling system. A critical factor in keeping the oxide concentration low is the reactor temperature. If pressure is the control mechanism, a low temperature in the reactor will allow the oxide to build to a potentially unsafe concentration. Concentration of unreacted epoxides is the cause of the greatest number of reactor failures. The problem becomes larger with propylene oxide and especially butylene oxide, where the vapor pressure of the oxide may not be a reliable indication of liquid phase concentration. The reactor should have a safety relief device sized to handle a runaway reaction due to loss of cooling. One of the authors has seen an autoclave and its high pressure cell catastrophically destroyed, with the autoclave top thrown many hundreds of feet. The cause was the inadvertent feeding of ethylene oxide at a low temperature, an error that allowed the accumulation of a large inventory of ethylene oxide. The uncontrolled polymerization that followed proved to be uncontainable.

To avoid exposure of personnel to unreacted ethylene oxide or propylene oxide, it is necessary to hold the reactor contents at temperature after the end of the feed until the concentration of unreacted epoxides has dropped to an acceptable level. This procedure is called a cook-out or digestion. A cook-out may be necessary during synthesis because the vessel will fill with liquid as the reaction proceeds and the polymer is produced. This will compress the nitrogen in the vessel, and the partial pressure of the monomer will therefore decrease (the system is run by keeping pressure constant). The reaction rates will fall to unacceptably low levels. Venting of the excess nitrogen after a cook-out will allow feed to be resumed at faster rates. It may even be necessary to remove some of the reactor's liquid contents to allow room for further reaction. This is most likely to occur during the synthesis of higher molecular weight products.

The commercial preparation of poly(alkylene oxides) is carried out in a manner analogous to that described for the laboratory autoclave. A semibatch stainless steel system with a recirculation loop and an agitator has been described. The reactions are carried out at 100–120°C at pressures of 60 psig. The oxide feed rate is controlled by pressure, and feed times are on the order of 15 hours or more [16].

Pressindustria Company has reported a novel method for synthesizing polyalkylene glycols [17]. The solution of growing polymer is sprayed through the headspace of a horizontal reactor. The reaction with oxide monomer is reported to take place at the gas–liquid interface. Rapid reactions without large increases in pressure or temperature are reported. Cooling takes place with an external heat exchanger.

The first commercial-scale syntheses were performed at the Union Carbide production facility in Charleston, West Virginia. The first preparations were similar to that used today. Sodium salts of alcohols were used as starters at reaction temperatures slightly above those used currently. Butanol was the starter alcohol of choice for monoethers. The products developed at this time form the backbone of the UCON® Fluids product line of Union Carbide and has been widely duplicated by other manufacturers. The method first used at Union Carbide to neutralize these fluids was unusual. The crude fluids were diluted with water, acidified with carbon dioxide, extracted with hot water, and then stripped of water at high temperature. Decolorizing with activated charcoal was the last step.

D. Preparation of Capped Polyalkylene Glycol

Polypropylene glycol dimethyl ether has become available as a commercial lubricant. This requires that the hydroxyl end groups be converted to the methyl ether:

$$\mathrm{ROH} \rightarrow \mathrm{ROMe}$$

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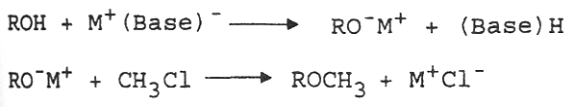
Although the conditions used commercially to effect this transformation are not reported, it is almost certainly done by a Williamson ether synthesis. This involves converting the alcohol to its alkoxide form, followed by reaction with methyl chloride:

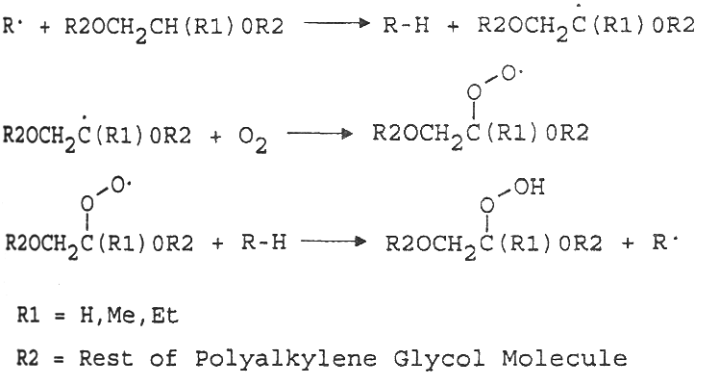


The art of this transformation is the conversion of the alcohol into its alkoxide. Sodium hydroxide is the most convenient base, and it works well for low molecular weight ethoxylates [18,19]. Higher molecular weight ethoxylates can be capped by means of sodium hydroxide and a phase transfer catalyst [20]. Propoxylates, which are secondary alcohols, hence more difficult to convert to their alkoxide form, are normally capped by adding sodium or potassium methoxide and driving the equilibrium reaction between the different alkoxide forms to the polyether alkoxide by removing the methanol [21]. Capping efficiency is limited by the difficulty of converting all the end groups to the higher energy alkoxide species. Improved yields can be obtained by using sodium hydride after the methoxide reaction has been driven as far as is practical [21] or by using sodium hydride alone [22].

E. Oxidative and Thermal Stability

The bond strength of the carbon–carbon bond is 84 kcal/mol (ethane), which is slightly stronger than the 76 kcal/mol carbon–oxygen bond of an ether (dimethyl ether) [22]. Other authors have reported that carbon–oxygen ether bonds are comparable to, or slightly stronger than, the usual carbon–carbon bonds [23]. However, from a thermochemical standpoint, polyalkylene glycols are usually considered less stable than typical hydrocarbons. In the absence of air, they can be used up to about 250°C.

The poly(alkylene oxides) are all polyethers with an oxygen atom in every third position of the polymer backbone. As with all ethers, a secondary or tertiary carbon adjacent to the ether oxygen is susceptible to oxidative attack. The mechanism involves a free radical abstraction of the hydrogen on the α carbon, resulting in a carbon-based radical stabilized by the adjacent oxygen atom. This can then react with oxygen to produce a peroxy radical. The chain process is continued, with the peroxy radical abstracting a hydrogen atom to give another oxygen stabilized radical:



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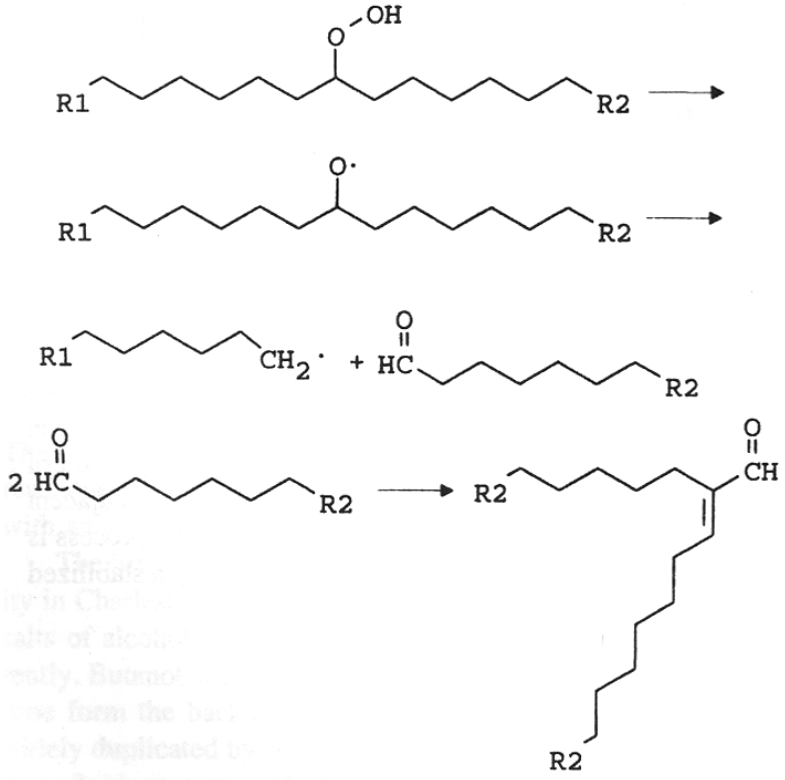
The process does not continue to build peroxide levels, since a number of mechanisms lead to peroxide destruction. In the early stages of oxidation the peroxide will increase, but as the reaction proceeds and carbonyl levels build, the peroxide level reaches a steady state. Further reaction will lead to the formation of acidic material. As the acidic oxidation products build, the viscosity begins to drop. Studies of the oxidation of polypropylene glycols [25] and polyethylene glycols [26] show that the polymers degrade into lower molecular weight products as they oxidize. This is in contrast to the behavior of petroleum products, which build higher molecular weight products as they oxidize [27]. It is these higher molecular weight materials that precipitate from the oil and produce sludge.

It is the fate of the hydroperoxides that determines the tendency of a lubricant to form sludge. In the case of petroleum, the hydroperoxides form hydrocarbon-based aldehydes, which can undergo aldol condensations to form high molecular weight α,β-unsaturated species that themselves are reactive [28]. This leads to the formation of high molecular weight polar species that are not soluble in the parent nonpolar base oil and therefore precipitate out of solution to form sludge.



The fate of hydroperoxides is different in polyalkylene glycols and in petroleum. Because every third atom is an oxygen, a high proportion of the chain cleavage products in the former case are esters. While esters can condense, the reaction is difficult and is unlikely to occur. The type of end groups can be determined by proton magnetic resonance. For polyethylene glycols, a prominent formate peak is formed at 8.1 ppm, indicating the following reaction:

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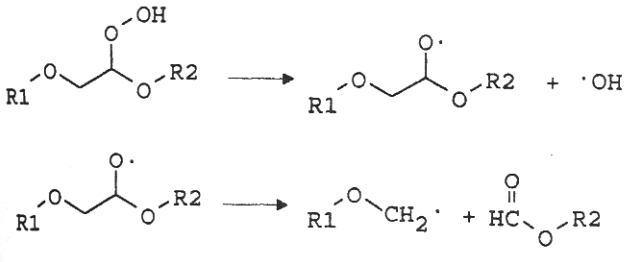

In the case of polypropylene glycols, the reaction products are more complex owing to the greater complexity of the molecules. The end groups produced are shown in Table 1 [25]. These end groups are not simple aldehydes and will undergo condensation with difficulty.

When sufficient degradation has taken place, volatile products will be produced. These have been quantified in the case of polypropylene glycol degradation [25], as shown in Table 2.

The oxidation of polyalkylene glycols yields polar, oxygenated products. Polyalkylene glycols themselves are polar and will dissolve these oxidation products. In contrast, oils are nonpolar and their oxidation products are polar, consisting of peroxides and carbonyl species as well. Oils will not dissolve these polar species, and this property contributes directly to their tendency to form sludge and varnish.

The tendency of polyalkylene glycols to solubilize their own degradation products, and their cleavage to form volatile species, can be cited to explain their low Conradson carbon and Ramsbotton carbon (ASTM D189 and D 524), typically less that 0.01%. When sludges do form from polyalkylene glycols, it is usually in oxygen-starved systems as a result of aldehyde condensation. Under conditions of exhaustive oxidation, the chain cleavage will have occurred to such an extent that the oxidation products evaporate. The volatilization of the fluid, together with the tendency not to form carbon or sludge, means that the polyalkylene glycol will be removed under high temperature applications in a property known as clean burn-off. Clean burn-off is important in a number of the applications for these products—for example, as a carrier for graphite on chains being used in ovens or kilns. As with the pyrolysis products of any organic material, good ventilation, should be installed to ensure the removal of the vapors from the workplace.

The oxidation of polyalkylene glycols could result in shorter than desired service life for some applications. Oxidation can effectively be controlled through the addition of antioxidants to interrupt the chain transfer oxidation mechanism [29]. Typical antioxidants that have been used include butylated hydroxyanisole, phenothiazine, hydroquinone monomethyl ether, butyl-

Table 1 End Group Analysis of Oxidized Polypropylene Glycol

Group	Chemical shift, δ (ppm)	O_2 consumed (mol/mol)
—COOH	—	0.02
Me—CO—CH_2—O—	2.1	0.4
MeCO—O—	2.0	0.2
H—CO—O—	7.95	0.3
Total—CO—	—	0.9

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Table 2 Volatile Products from Oxidation of Polypropylene Glycol per Mole of Absorbed Oxygen

	Yield (mmol) at:			
Product	95°C	110°C	125°C	140°C
Water	514	775	896	877
Acetaldehyde	8.82	12.4	14.4	17.5
Acetone	1.24	1.66	1.86	2.47
Methanol	0.0176	0.0248	0.0283	0.0334
Formaldehyde	1.13×10^{-3}	0.92×10^{-3}	1.21×10^{-3}	2.81×10^{-3}
Methane	13.5	12.4	10.4	16.6
—OOH residue	340	150	0	0
Total	878	951	923	913

ated hydroxytoluene [30], and phenyl-α-naphthylamine [31, p. 109]. The poly(alkylene oxides) are dramatically stabilized toward oxidation by the addition of antioxidants. In many cases antioxidants at levels of a few hundred parts per million are sufficient to stabilize against oxidative degradation under mild conditions and higher levels will stabilize these systems under much more severe conditions. The uses of inhibited polyalkylene glycols as heat transfer fluids and as gear and calender lubricants are all examples of successful high temperature applications. These applications show that if the system is protected against oxidative attack, either by the addition of an antioxidant or by removal of oxygen, polyalkylene glycols will have very good high temperature stability.

F. End Group Chemistry

The polyalkylene glycols all have at least one hydroxyl group on the end of the molecule. If they have been produced from water or a multifunctional starter, they will have more than one hydroxyl group. The polyols used for urethane applications perform by virtue of the reaction of the hydroxyl groups reacting with isocyanate groups to give the urethane linkage. In this application, stearic factors cause the primary hydroxyl group to be more reactive than a secondary hydroxyl. The urethane polyols are formed from propylene oxide. Since this results in a less reactive secondary hydroxyl end group, it is necessary to end-cap the polyol with a small amount of ethylene oxide to increase the number of primary alcohol terminated molecules.

Other end group reactions are used to functionalize polyalkylene glycols. These reactions use the known alcohol derivatization reactions. Esters are formed by reaction with either organic or inorganic acids. In addition to the etherification reactions already discussed, it is possible to react the alcohol with a strong acid and an olefin to give an alkyl ether cap.

Other derivatization reactions of the alcohol end group are possible. It has been reported that poly (dichlorophosphazene) can be reacted with polyalkylene glycols to give poly(phosphazene) derivatized with grafted polyalkylene glycol chains [32]. These materials are reported to have utility as metalworking lubricants.

G. Coordination Chemistry

The presence of an ether oxygen atom at every third position of the polymer backbone leads to the rich coordination chemistry of these compounds. The use of these polymers as phase transfer agents has been reviewed [33]. Complexation with phenols, phenolic resins, bromine,

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iodine, gelatin, sulfonic acids, mercuric slats, tannic acid, poly(acrylic acid), and urea all have been reported [34]. The use of poly(ethylene oxide) polymers as flocculation agents is related to their absorption on colloidal silica, clay, and minerals.

The facile wetting of metal parts in lubrication applications is related to the ability of the polymer to associate with me metal surface. Like the complexation of other chemical species, the ability of the polyalkylene glycol to wet a metal surface is due to the presence of an ether oxygen atom at every third position of the polymer chain. This results in good extreme pressure and metalworking performance. The solution properties of these polymers in water are also directly related to the association of the water with the ether oxygen atoms.

IV. PHYSICAL PROPERTIES

A. Base Fluids

The physical properties of poly(alkylene oxides) are best understood by considering them as a series of homologous derivatives. Thus the polymers derived exclusively from ethylene oxide are considered as members of one class differing primarily in molecular weight. The trends in properties can then be understood in relationship to structure.

The properties of the ethylene oxide polymers derived in principle from water (diols identified as PEGs) or from methanol [35] (identified as methoxy PEGs) are listed in Table 3. As these data indicate, the poly(alkylene oxides) with a molecular weight above about 600 are crystalline solids. The alcohol-started products follow the same pattern. The structure in the solid state has been examined by infrared, x-ray diffraction, and Raman spectroscopy. It has

Table 3 Properties of Polyethylene Glycols

Molecular weight	Specific gravity, 20/20°C	Melting or freezing range (°C)	Solubility in water at (20°C/wt %)	Viscosity at 99°C (cSt)
Polyethylene glycols				
200	1.127	−65[a]	Complete	4.3
300	1.127	−15 to −8	Complete	5.8
400	1.128	4–8	Complete	7.3
600	1.128	20–25	Complete	10.5
1000	1.101[b]	37–40	70[c]	17.4
1450	1.102[b]	43–46	70[c]	25–32
3350	1.072[d]	54–58	62[c]	75–110
4600	1.073[d]	57–61	50[c]	160–230
8000	1.075[d]	60–63	50[c]	700–900
Polyethylene glycol monomethyl ethers				
350	1.097	−5 to 10	Complete	4.1
550	1.078[b]	15–25	Complete	7.5
750	1.084[b]	27–32	Complete	10.5
2000	1.20	49–54	68[c]	63
5000	1.20	57–63	58[c]	613

[a] Sets to a glass.
[b] At 55/ 20°C.
[c] Approximate, homogeneous pastes or solids at this temperature.
[d] Density (g/mL at 80°C).

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been concluded that the molecules exist in a helical structure. The high symmetry of the structure leads to high crystal packing energies that favor crystallization. Although polyethylene glycols (PEGs) are soluble in water in all proportions, the phase of the solution may be solid or liquid. For instance, PEG-8000 will form a homogeneous liquid with water in all proportions above its melting point, but if the concentration of PEG-8000 is above 50%, the solution will freeze or become a paste at room temperature.

The physical properties of the polymers of propylene oxide [36] are given in Table 4. These are derived from a butyl alcohol starter. In contrast to the polymers of poly(ethylene oxide), these polymers do not readily crystallize. Instead, they become too thick to flow at a temperature known as the pour point. The pour point for these polymers is very low. Even at temperatures below their pour point they do not crystallize but form a glasslike solid. The pendant methyl group on the backbone breaks up the crystal packing. These polymers have very high viscosity indices.

The random copolymers of ethylene oxide and propylene oxide have the properties [36] listed in Table 5, which gives data for two families of structurally related compounds. The monobutyl ethers polymers are derived from a butyl starter and are formed from equal weights of ethylene oxide and propylene oxide. The diol polymers are derived from water, giving them two hydroxyl groups. The oxide incorporated in these is 75 wt % ethylene oxide and 25 wt % propylene oxide. The copolymers derived from equal amounts of ethylene oxide and propylene oxide have very low pour points. If we compare the pour points of these random copolymers with those of the polymers derived from propylene oxide, we find the values very similar. In fact, the copolymers seem to have slightly lower pour points at the higher molecular weights. This may be due to the slightly higher symmetry of the homopolymers of propylene oxide compared to the mixed copolymers. These copolymers have even higher viscosity indices than was the case with the polymers derived only from propylene oxide. The random copolymers derived from block feeds of ethylene oxide and propylene oxide have physical properties that are dependent on the relative size of each block as well as the total molecular weight. Commercially available products are derived from poly(propylene glycol), which is then reacted with ethylene oxide. Alternatively, a poly(ethylene glycol) molecule can be reacted with propylene to produce what is referred to as a reverse blocked structure. These products are available as liquids, pastes, or flakable solids.

Butylene oxide polymers are available as either diols or monobutyl ethers. These have the

Table 4 Physical Properties of Polypropylene Glycol Monobutyl Ethers

Molecular weight	Viscosity at 40°C (cSt)	ISO grade	Viscosity index	Pour point (°C)	Specific gravity, 20/20°C	Flash point, Pensky–Martins closed cup (°C)
340	11	10	83	−56	0.960	119
640	28	—	161	−48	0.980	177
740	34	32	169	−46	0.983	190
1020	61	—	184	−40	0.990	179
1240	80	—	190	−37	0.993	177
1420	100	100	196	−34	0.995	185
1550	120	—	200	−32	0.999	168
2080	230	220	214	−29	0.999	190
2490	370	320	219	−23	1.011	188

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Table 5 Physical Properties of Ethylene Oxide/Propylene Oxide Copolymers

Molecular weight	Viscosity at 40°C (cSt)	ISO grade	Viscosity index	Pour point (°C)	Specific gravity, 20/20°C	Flash point, Pensky–Martens closed cup (°C)
50:50 Ethylene oxide/propylene oxide, monobutyl ether						
270	8.3		97	−57	0.971	90
520	19		165	−48	1.013	141
750	33	32	197	−46	1.028	186
970	53		212	−40	1.036	194
1,230	81		220	−37	1.041	204
1,590	130	160	230	−34	1.046	202
2,660	398		254	−32	1.056	172
3,380	700	680	269	−29	1.058	172
3,930	1,020	1000	281	−23	1.063	180
75:25 Ethylene oxide/propylene oxide, diol						
980	60	100	184	−15	1.103	188
2,470	290	320	207	−7	1.100	219
15,000	17,000		414	4	1.093	191

physical properties [37] shown in Table 6. In general, the butylene oxide monobutyl ethers have lower viscosities and lower viscosity indices compared to the same molecular weight ethylene oxide/propylene oxide (EO/PO) copolymer or propylene oxide polymer. This is to be expected, since the polymer chains are not as long (fewer repeating units) for the same molecular weight.

Copolymers of propylene oxide and α-olefin epoxide monoalkyl ethers have the properties shown in Table 7 [38,39]. Intermediate viscosity grades are available by blending these two fluids.

Table 6 Properties of Butylene Oxide Polymers

Molecular weight	Viscosity at 40 °C (cSt)	Viscosity index	Pour point (°C)	Density at 25°C (g/Ml)	Flash point, Pensky–Martens closed cup (°C)
Butylene oxide polymers, diols					
500	39.4	3	−30	0.975	>350
1000	86.9	118	−26	0.971	>350
2000	209.7	142	−26	0.970	>350
4800	731.4	189	−21	0.971	>350
Butylene oxide polymer, monobutyl ethers					
500	17.7	106	−56	0.942	>350
1000	50.9	167	−35	0.955	>350
1500	105.9	153	−30	0.961	>350
2000	185.0	164	−33	0.963	>350

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Table 7 Physical Properties of Propylene Oxide- and α-Olefin Epoxide Monoalkyl Ethers

Viscosity (cSt)		Viscosity	Pour	Density at	Flash point, Cleveland
At 40°C	At 100°C	index	point (°C)	20°C (g/mL)	open cup (°C)
220	27	170	−28	0.975	260
640	39.1	100	−8	0.978	>240

A typical polypropylene glycol dimethyl ether used for lubrication has properties shown in Table 8 [40].

Viscosity index, the measure of the change in viscosity with temperature, is very much dependent on polymer structure. In linear polymers, which comprise the major base fluids used in lubrication, the viscosity index depends on the end groups and on which oxides are used in synthesis. The end group effects can be seen by looking at Table 9, which shows the effect of viscosity index on polypropylene glycol polymers that are isoviscous at 100°C [41]. This effect is almost certainly due to hydrogen bonding among the hydroxyl groups at low temperature. This weak effect, which will serve to make the effective molecular weight seem larger and the polymer more viscous, will be broken up with the addition of thermal energy. Thus we see that it takes a smaller molecule to achieve a target viscosity at low temperature if that molecule has hydroxyl groups.

For fluids isoviscous at 100°C, the viscosity index decreases as the number of carbon atoms in the epoxide monomers increases. Thus, substituting propylene oxide for ethylene oxide decreases the viscosity index, as will substituting butylene oxide for propylene oxide. This can be seen for a series of isoviscous dimethyl capped polyethers shown in Table 10 [41].

Although the molecular weights are not given in the preceding examples, for the EO/PO copolymers, isoviscous polymers at 40°C have the same molecular weight whether they are polypropylene glycol monobutyl ethers or EO/PO monobutyl ether copolymers. This means that the polypropylene glycol monobutyl ether molecule is shorter. Shorter molecules cannot unfold as far at increased temperature, giving a lower degree of chain entanglement and viscosity. This is the probable reason for the viscosity index observations in Table 10.

The film-forming properties of lubricants are critical. Under extreme pressure, lubricating materials tend to thicken. This behavior is important in keeping a liquid layer between the parts being lubricated. The change in viscosity with pressure is defined by the pressure–viscosity coefficient α, defined as follows:

$$\alpha = \frac{d \ln \eta}{dP}$$

The pressure–viscosity coefficient has been determined for a series of polyalkylene glycols [42]. The results are shown in Table 11. For reference, typical petroleum oils have pressure–viscosity

Table 8 Properties of Polypropylene Glycol Dimethyl Ether

Viscosity at 40°C, cSt	49.99
Viscosity at 100°C, cSt	10.34
Viscosity index	214
Pour point, °C	< −50

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Table 9 Effect of End Group on Viscosity Index

Chemical structure	Viscosity at 100°C (cSt)	Viscosity index
HO $(CH_2CH(CH_3)O)_xH$	9.607	137
$HO(CH_2CH(CH_3)O)_xMe$	9.816	179
$MeO(CH_2CH(CH_3)O)_xMe$	9.760	214

Table 10 Viscosity Index of Polyalkylene Glycol Dimethyl Ethers

Monomers used to synthesize[a]	Viscosity at 100°C (cSt)	Viscosity index
EO	9.960	245
EO/PO = 7/3	8.575	229
EO/PO = 5/5	11.04	227
EO/PO = 3/7	9.760	225
PO	9.760	214
PO/BO = 7/3	10.84	195
PO/BO = 5/5	10.92	187
BO	9.388	157

[a] Ratios are mol ratios.

Table 11 Pressure–Viscosity Coefficient, α, for Selected Polyalkylene Glycols

Structure	Structure of test polymers (%)			Viscosity at 20°C (%)	α at 22°C (GPa^{-1})
	EO	PO	BO		
Monobutyl ether	75	25	—	190	9.1
Monobutyl ether	50	50	—	151	9.9
Monobutyl ether	—	100	—	70	14.8
Monobutyl ether	—	100	—	86	13.5
Monobutyl ether	—	100	—	180	13.9
Monobutyl ether	—	100	—	364	14.3
Monobutyl ether	—	100	—	604	14.6
Diol	—	100	—	65	14.8
Monobutyl ether	—	—	100	239	14.9
Monobutyl ether	—	—	100	559	15.7
Diol	—	—	100	573	15.2
Triol	—	—	100	1247	7.7

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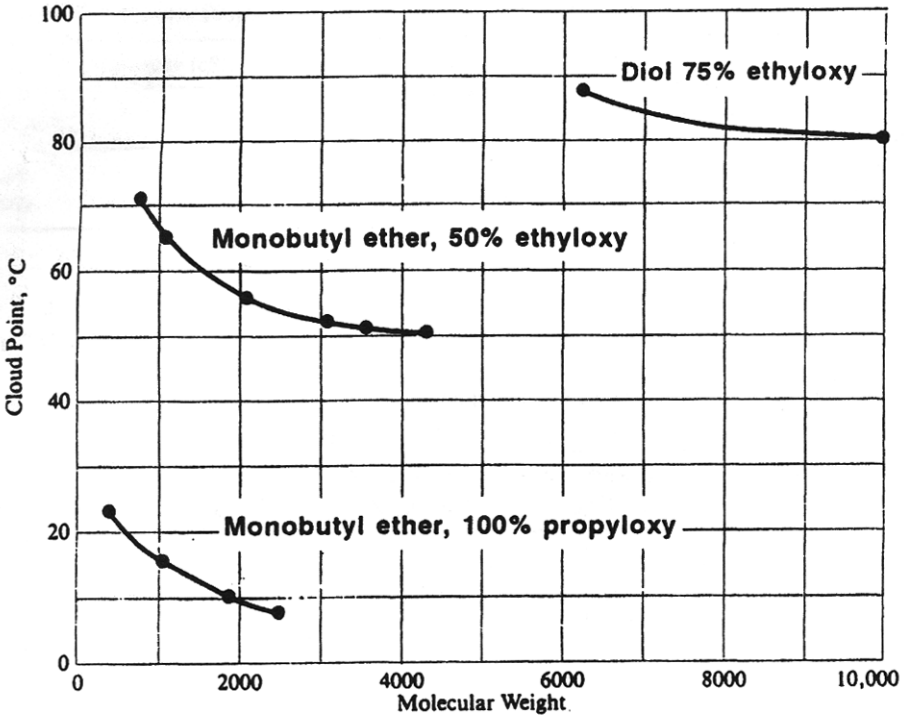

Figure 1 Cloud point for common polyalkylene glycols, as determined with 1% polymer in water.

coefficients between 21 and 33 [43]. The results of Table 11 show that the pressure–viscosity coefficient for linear polymers increases in the monomer order BO > PO > EO.

The results in Table 11 suggest that propylene oxide polymers will be better lubricants than EO polymers. Yet, tests under boundary lubrication conditions showed that improved friction and wear behavior was found in EO/PO polymers as the amount of EO was increased [43]. In all cases, with or without additives, the polyalkylene glycols outperformed the petroleum test fluids. All polyethers tested reached load levels of 10 or more without EP additives in the FZG test, promulgated by the German standard-making body (A/8, 3/90 DIN 51 354). Other workers [44] report load levels of 12 with polyalkylene glycols in the FZG gear test (A/16, 6/140). It may be that the pressure–viscosity coefficient is important only in extreme pressure applications, such as heavily loaded ball bearings. Under less stressful applications, such as gears, the increased polarity provided by ethyloxy groups will allow greater interaction with the polar metal oxides that exist on metal surfaces. This may give the molecules their mild extreme pressure additive qualities.

B. Solution Properties

The aqueous solution properties of polyalkylene glycols are critical for many of their commercial applications. Polyalkylene glycols show the property of inverse solubility. In other words, their solubility in water decreases as the solution temperature rises. At a temperature known as the cloud point, the polyalkylene glycol comes out of solution and forms a turbid, or cloudy, dispersion.

For copolymers of ethylene oxide and propylene oxide and the propylene oxide homopoly-

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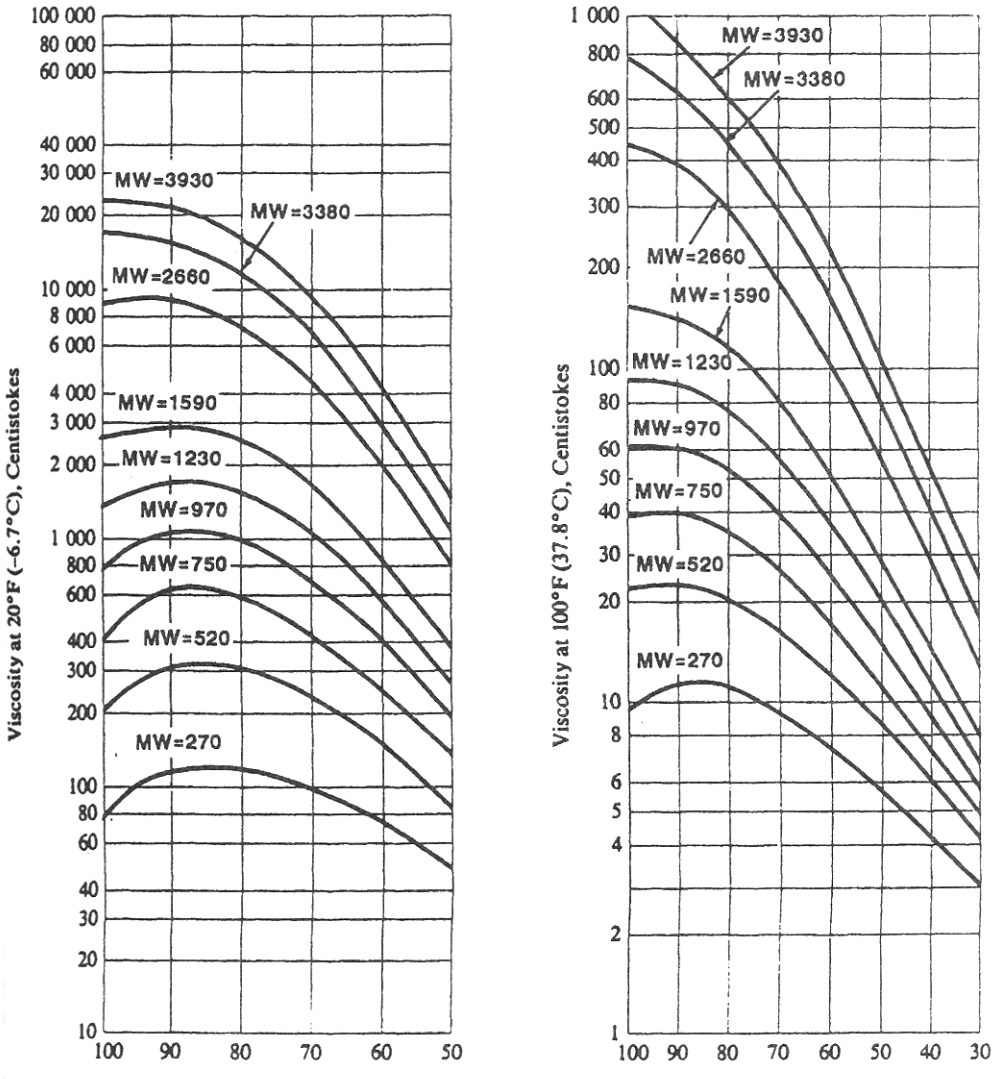

Figure 2 Viscosity of water/polyalkylene glycol solutions at two temperatures.

mers, the cloud point is a function of molecular weight and the proportion of ethylene oxide used in the synthesis. Increasing the molecular weight in an otherwise similar polyalkylene glycol series lowers the cloud point. Raising the amount of ethylene oxide relative to propylene oxide in the synthesis of polyalkylene glycols of otherwise similar structure raises the cloud point. Cloud point is very sensitive to salt concentration, which lowers the cloud point. The cloud point is generally below room temperature for the homopolymers of propylene oxide. They are generally not considered soluble in water, although the lower molecular weight examples are readily dissolved in cold water. The cloud points for common polyalkylene glycols are shown in Fig. 1. Butylene oxide polymers will have a greater degree of water insolubility than the propylene oxide polymers because of their decreased oxygen content.

The cloud point is an important property in metalworking applications. Water-based metal-

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Table 12 Separation Temperatures of Aqueous 50:50 EO/PO Monobutyl Ether, Molecular Weight 970

Polyalkylene glycol (vol %)	Separation temperature (°C)
1	65
10	47
20	47
30	49
40	53
50	54
60	57
70	62
80	72
90	>100

working fluids often contain 1–5% polyalkylene glycol. When the polymer is exposed to the high temperature of the working surface, it comes out of solution to provide the lubricity needed.

The hydration of polyalkylene glycols in aqueous solutions has been examined by differential scanning calorimetry. The more water-soluble poly(ethylene oxide) polymers were found to coordinate 2.8 moles of water per ether linkage (2.9 by molecular dynamics calculation [45]), while the copolymers derived from equal weights of ethylene oxide and propylene oxide coordinated to 2.4 moles and the homopolymers from propylene oxide coordinated with only 1.6 moles [46]. Water of hydration is responsible for water solubility, and its presence explains why propylene oxide polymers are of limited water solubility but ethylene oxide/propylene oxide copolymers have extensive water solubility. All ethylene oxide polymers are believed to be heliform in water, with hydration inside the helix. At elevated temperatures, the helix is believed to elongate, upsetting the hydration and leading to insolubility [45].

The hydration of the ether linkages affects the solution viscosities. Small amounts of water will actually raise the viscosity owing to an increase of the effective molecular weight. This

Table 13 Freezing Point of Aqueous 50:50 EO/PO Monobutyl Ether, Molecular Weight 970

Polyalkylene glycol (vol %)	Freezing point (°C)
10	0
20	0
30	−1
40	−2
50	−7
60	−10
70	−11
80	−28
90	<−65

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Table 14 Solubilities of Polyalkylene Glycols in Common Solvents

	1 part PAG, 9 parts Solvent[a]			1 part solvent, 9 parts PAG[a]		
Solvent	Water-insoluble PAG[b]	Water-soluble PAG[c]	Water-soluble PAG[d]	Water-insoluble PAG[b]	Water-soluble PAG[c]	Water-soluble PAG[d]
Acetone	S	S	S	S	S	S
Cyclohexane	S	I	I	S	S	S
Butyl ether	S	S	I	S	S	S
Glycerol	S	S	S	S	S	S
Heptane	I	I	I	I	S	S
Isopropanol	I	I	I	I	I	I
Methanol	S	I	I	S	S	I
2-Octanol	S	S	S	S	S	S
Toluene	S	S	S	S	S	S
Dichloroethane	S	S	S	S	S	S
Ethylene glyol	S	S	S	S	S	S

[a] S, soluble; I, insoluble.
[b] PAG is polypropylene glycol, monobutyl ether, MW = 1550.
[c] PAG is 50:50 ethylene oxide/propylene oxide copolymer, MW = 1590.
[d] PAG is 75:25 ethylene oxide/propylene oxide copolymer, MW = 2470.

effect is decreased at elevated temperatures, the result of thermal energy breaking the water–ether association. The viscosity of water/polyalkylene glycol solutions at two temperature is shown in Fig. 2.

Solutions of polyalkylene glycols at temperatures above their cloud point will separate into a water-rich layer and a layer rich in polyalkylene glycol. The separation temperatures for an EO/PO monobutyl ether are given [36] in Table 12. The thermal separation of polyalkylene glycols from water can be a useful way of concentrating them from aqueous waste streams for disposal.

Because of the strong hydrogen bonding of water to polyalkylene glycols, the freezing point of water in these polymers can be decreased. This can be seen in Table 13 [36], which gives the freezing point for each of nine polyalkylene glycol/water solutions. Table 13 shows that up to 10% water can be absorbed by a polyalkylene glycol without crystal formation by the water. This property is important in uses like brake fluids, where water crystals would cause the system to fail.

C. Solubilities

The solubility of a polyalkylene glycol is determined by its structure. All polyalkylene glycols are polar molecules and will dissolve in polar solvents. The solubility of molecules derived from ethylene oxide will have water solubility and will be insoluble in nonpolar solvents. The solubility of molecules derived from propylene oxide will be water insoluble, and will dissolve, at least to some level, in nonpolar solvents. Molecules derived from butylene oxide or higher oxides will have increased oil solubilities and are manufactured to take advantage of this property. Table 14 gives the solubilities of molecules derived from EO/PO and PO [36].

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V. MANUFACTURE AND MAJOR USES

A. Manufacturers

In the United States, the largest producer of polyalkylene glycols is Union Carbide Corporation. Other producers include Dow, Olin, and Huntsman. In Europe, the largest producer is Inspec, with ICI being almost as large. In Asia, Nippon Oil and Fat is the largest producer. Other Asian producers include Sanyo and Idemitsu.

Dow is the sole producer of butylene oxide polymers.

Inspec is the sole producer of the oil-soluble propylene oxide/α-olefin epoxide copolymers.

The polypropylene glycol dimethyl ethers are not available as base fluids. Idemitsu uses them internally.

B. Major Uses

Polyalkylene glycols have found use as petroleum lubricant replacements when the cost is justified by a performance advantage. Polyalkylene glycols differ from petroleum lubricants of similar viscosity in the following respects:

1. Lower pour point
2. Higher viscosity index
3. Lower tendency to form tar and sludge
4. Increased solvency
5. Wider range of solubilities, including water solubility
6. Higher flash point
7. Lower vapor pressure
8. Lower ash and metals content
9. Possess cloud points

Comparison of polyalkylene glycols with petroleum should be done case by case, since petroleum lubricants can be formulated many different ways. Polyalkylene glycols owe their commercial existence to the ability to do what petroleum products cannot.

Changing from petroleum lubricants to polyalkylene glycol can present special problems. Machinery that has been used with petroleum often has wear grooves filled with carbonaceous material. Because of the good solvency characteristics of polyalkylene glycols, this carbonaceous material is often removed on changeover, revealing wear scars that had not been visible earlier. This wear is then incorrectly attributed to the polyalkylene glycol. Petroleum-derived sludge can also be softened and result in clogged filters.

Although polyalkylene glycols are compatible with most elastomers, this area should be evaluated before changeover. Polycarbonate and polyurethane machine parts are sometimes softened or embrittled. Polycarbonates are often used as site glasses on lubricant reservoirs.

The good solvency properties tend to result in softened and lifted paint. In the case of exterior paint, this is a cosmetic issue. Catalyzed epoxy, epoxy-phenolic, or modified phenolic coatings have performed well in contact with polyalkylene glycols. In the case of interior paint, the lifted coating can result in clogged filters and orifices if care is not taken during the conversion process.

1. Fire-Resistant Hydraulic Fluids

Fire-resistant hydraulic fluids are used wherever fires cannot be tolerated. Fire-resistant fluids are used in areas like foundries, die-cast aluminum facilities, steel mills, and mines. The tradi-

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tional classes of fire-resistant hydraulic fluids are the polyalkylene glycol based water glycol fluids, oil-in-water emulsions, phosphate esters, and polyol esters.

Fire-resistant hydraulic fluids can be formulated from polyalkylene glycols. These are the so-called water–glycol fluids. They are formulated as follows:

Component	Purpose
Water	Fire protection
Glycol	Freeze protection and some thickening
Polyalkylene glycol	Provides viscosity
Antiwear additive	Provides mixed film and boundary lubrication
Corrosion inhibitors	Headspace and liquid corrosion protection

Fire resistance of hydraulic fluids is measured by standard tests [47]. The most widely used of these are the spray flammability test and the hot channel test, industry standard tests run by Factory Mutual Corporation. In the spray flammability test, an aerosol of the test fluid is sprayed through a flame. The following results are obtained [48]:

Petroleum-based hydraulic fluids burned with a large flame while the oil was being sprayed. Combustion continued after the ignition source was removed.

Both polyol ester and phosphate ester burned while being sprayed through the ignition source. The burning stopped when the ignition source was removed. This is considered to be a passing result.

Water/glycol fluids did not burn when sprayed through the ignition source.

In the hot channel test, hydraulic fluid is sprayed onto a steel channel heated to 704°C and inclined at 30 degrees. This test is used to evaluate spillage of the test fluid onto a heated surface. The various classes of lubricants have the following results [47]:

The petroleum-based hydraulic fluid burned with a very large flame.

The phosphate ester did not burn with a flame, but did emit large volumes of white smoke.

The polyol ester burned like the oil while being sprayed, but the burning stopped when the spray stopped.

The water/glycol fluid burned with a reduced flame.

Both the polyol ester and the phosphate ester passed me test, which calls for the fluid to stop burning 5 seconds after the spray of hydraulic fluid stops. They still exhibit fire-related risks (smoke, flames), which are greatly reduced in the case of the water/glycol fluid.

Part of the reason for the superior fire resistance of water/glycol fluids lies in the lower heat content of the fluids. Table 15 gives the heat contents for some typical water/glycol fluids [48]. Not only do the water/glycol fluids have to evaporate water until the organic portion is left, but the organic portion consists of materials that have lower heat values because of their polyether structures. Essentially, the polyether structure means that such a compound is already partially burned.

Water-in-oil emulsions, with water contents of 80%, show fire-resistant performance most similar to that of water/glycol fluids. They are lower in viscosity, and as a result should be used in pumps with narrower tolerances, requiring the use of better filtration to prevent particles from damaging the moving parts. The lower viscosity also leads to higher pump wear. Because they

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Table 15 Heat Content of Hydraulic Fluids

Fluid type	Heat content gross (kJ/g)	Total heat output (kJ/g)
Mineral oil	44.9	14.1
Water-in-oil emulsion	25.7	8.5
Phosphate ester	45	6.7
Water/glycol	13	2.7

have water contents as high as 80%, their upper temperature limit of use is 60°C owing to the vapor pressure of the contained water. They are prone to microbial degradation, and use of biocides in the machinery should be considered.

The wear rates obtained for water/glycol fluids have improved dramatically over the years, as indicated in Table 16 [49]. These tests were run according to a German standard (DIN 51, 389 E) using a Vickers V-104C vane pump for 250 hours at 1500 psi and 1500 rpm.

Because of their high water content water/glycol fluids have been traditionally limited to about 2000 psi operating pressure. Recently, high performance water/glycol fluids have been developed [48,50]. These fluids can operate at pressures at least 5000 psi. In addition to higher pressures and excellent fire resistance, the fluids show low wear rates as well. Table 17 compares typical wear rates for several types of hydraulic fluid [48]. These tests were run according to ASTM D-2882 for a duration of 100 hours at 2000 psi and 1200 rpm using a Vickers V-104 vane pump. The pass test criterion is 1 mg/h wear rate.

Water/glycol fluids show Newtonian behavior. They do not thin out with shearing, which can reach 10^6 s^{-1} in hydraulic pumps [49]. BASF tried to market a higher water content fluid using a novel polyalkylene glycol based thickener. The polyalkylene glycol contained a hydrophobic end group that resulted in associative thickening in the aqueous environment [51]. These fluids suffered from excessive shear thinning and high pump wear.

Water/glycol-based hydraulic fluids thickened with polyalkylene glycol are formulated in the viscosity region of low to medium viscosity oils. Their use temperature is limited from about −30 to 65°C. The upper temperature limit is a result of the high vapor pressure of the contained water. Higher temperatures can lead to cavitation and premature pump failure. These fluids generally have good seal compatibility.

To achieve optimal performance of water/glycol fluids, proper maintenance is essential [52]. Water content must be controlled to the specification level. Too little water will significantly raise the viscosity. Too much water will thin viscosity and also result in significant increases in wear. Water content is easily measured by refractometry. The amine, or alkalinity, content must also be monitored. Higher wear can be experienced if the alkalinity is above the

Table 16 Historical Wear Rates of Water/Glycol Fluids

	Total wear (mg)
1955–1965	4700–15,100
1965–1970	1300–2800
1970–1974	300–1100
After 1974	Approximately 100
Mineral oil	<100

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Table 17 Wear Rates of Different Hydraulic Fluid Types

Hydraulic fluid type	Wear rate (mg/h)
Conventional water/glycol fluid	0.65
Phosphate ester	0.05
Polyol ester	0.10
Antiwear oil	0.24
High performance water/glycol fluid	0.10

desired value. Greater wear will result if alkalinity is below the desired value. Alkalinity is easily monitored through acid–base titrations.

The maintenance problems with phosphate esters are different. The phosphate esters are the only widely used nonaqueous fluids employed as fire-resistant hydraulic fluids. These are triaryl and trialkyl esters of phosphoric acid. Like all esters, they are subject to hydrolysis back to their parent acid. Hydrolysis rate depends on structure, with the longer alkyl chain esters being the most resistant. They are frequently used with a bleaching clay filter to remove the acidic hydrolysis and oxidation by-products.

2. Brake Fluids

The use of polyalkylene glycols as the hydraulic fluid in braking systems for motor vehicles was one of the early uses of polyalkylene glycols. The properties that made them valuable were water miscibility, low pour point, high viscosity index, high boiling point, good elastomer compatibility, and low vapor pressure. Glycol ethers are commonly added, as are rust inhibitors and antioxidants.

The ability to absorb water is the property most useful in this application. At low temperatures, ice crystals would prevent the operation of the breaking system. At high temperatures, water could vaporize, causing "vapor lock." Even with the tendency to absorb water, the vapor lock temperature drops by about 80°C when the anhydrous system picks up 2% water [31, p. 328]. Water increase at low temperature increases the viscosity of the fluid. The lower the temperature, the greater the effect. This effect is due to hydrogen bonding, which is a weak interaction favored at reduced temperatures.

Silicone brake fluids are the only significant alternative to the polyalkylene glycol fluids. They have been utilized for their greater temperature stability in the newer generation of cars that have higher under-the-hood and brake operating temperatures. Their main disadvantages are higher cost and a water tolerance below that of the polyalkylene glycol based fluids. The two types of brake fluids are mutually insoluble, and it is important not to mix them. If the two types are mixed, the additives tend to partition between the two phases so that neither phase is properly protected against corrosion. Brake failure can result.

3. Compressor Lubricants

The compression of petroleum-derived gases such as methane, ethane, and ethylene presents a severe lubrication challenge. These process gases dissolve in petroleum and petroleum-like lubricants, serving to reduce the viscosity of the lubricant. As a result, very viscous petroleum oils are used, to induce the process gas to thin the lubricant to the desired viscosity at the use temperature. Unfortunately, this makes start-up, especially under cold conditions, very difficult. In addition, if the process gas contains higher petroleum fractions that reach their dewpoint

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when compressed, droplets will form that will wash the cylinder wall, leaving it essentially unlubricated.

Compared to other lubricants, hydrocarbon gases have greatly reduced solubility in the water-soluble polyalkylene glycols. Some examples are shown in Table 18 [53]. Other process gases that have been used successfully include hydrogen, carbon dioxide, landfill gas, and propane. Common benefits are reduced wear, cleaner systems, reduced maintenance, and reduced lubrication rates.

A few manufacturers market polyalkylene glycol based air compressor lubricants. This use depends on additive technology to limit air oxidation, is primarily limited to petroleum products.

4. Textile Lubricants

Water-soluble polyalkylene glycols are widely used in the textile industry. They are non-staining and can be washed from the finished yarn or fabric with water [54]. Polyalkylene glycols, when they are oxidized at moderate temperature with an adequate oxygen supply, do not form colored by-products. This property is particularly advantageous in the textile industry, where color is a critical quality consideration.

The same property that makes polyalkylene glycols useful as lubricants for fibers makes them important machine lubricants in the textile industry. If they come into contact with the textiles being worked, they are easily washed off. However, they tend to cause crazing of polycarbonate sight glasses.

5. Calender Lubricants

Petroleum meets the need of lubricating the large-diameter journal bearings, antifriction bearings, and gears that are present in mills and calenders used by the rubber, textile, paper, and plastics industry up to temperatures of 350°F. Above 350°F, petroleum products tend to form sludges, calling for increased maintenance. Polyalkylene glycols have been used in this application, since they do not tend to form sludge or carbon deposits.

6. Metalworking Fluids

Polyalkylene glycols are often used as lubricity additives in water-based cutting and grinding fluids [55,56]. In addition, they have been utilized in drawing, forming, stamping, and rolling lubricants [57–59]. Because of their good water solubility, polyalkylene glycols are most often used in "synthetic" metalworking fluids. These fluids form true solutions in water. Synthetic metalworking fluids based on polyalkylene glycols provide good lubricity and are excellent coolants. In general, they are also more resistant to microbial attack and easier to maintain that "soluble oil" metalworking fluids, which are actually oil-in-water emulsions [60].

Table 18 Solubilities of Process Gases at 4000 psi at 50°C of Common Lubricants

Lubricant	Process gas	Solubility (wt/%)
Polyalkylene glycol	Methane	2.9
Poly(α-olefin)	Methane	5.8
Polyalkylene glycol	Nitrogen	4.3
Poly(α-olefin)	Nitrogen	8.8
Polyalkylene glycol	Ethylene	7.8
White oil	Ethylene	14.1
Polybutene	Ethylene	13.8

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Polyalkylene glycols provide good lubricity in synthetic metalworking fluids by taking advantage of their inverse solubility in water [55,56]. At ambient temperatures, polyalkylene glycols are water soluble. At an elevated temperature, known as the "cloud point," the polyalkylene glycol becomes insoluble and forms small polymer droplets. When a synthetic metalworking fluid containing a polyalkylene glycol is brought into contact with a hot die or cutting tool, it is heated to a temperature above the cloud point of the polymer. The polyalkylene glycol then comes out of solution. The resulting polyalkylene glycol droplets coat the surfaces of the hot die or cutting tool, forming a lubricant film that provides excellent hydrodynamic lubricity.

Synthetic metalworking fluid formulations often contain both polyalkylene glycols and water-soluble boundary or extreme pressure additives such as fatty acids or phosphate esters. Combinations of polyalkylene glycols and fatty acids or phosphate esters have been shown to be synergistic, providing better lubricity than equivalent concentrations of either additive by itself [56]. As a result of this synergy, these aqueous metalworking fluids provide excellent lubricity as well as the good cooling properties of water [60]. Synthetic metalworking fluids will also contain other additives such as corrosion inhibitors, antifoams, and biocides.

7. Refrigeration Lubricants

A major new application for polyalkylene glycol (PAG) lubricants is in vehicle air conditioning (A/C) systems. All new air-conditioned cars and trucks sold in North America contain refrigerant R-134a and PAG lubricants in their A/C systems. All major car makers are also recommending PAG lubricants for the retrofitting of vehicles from refrigerant R-12 to R-134a. In 1987 the Montreal Protocol initiated a program to phase out the production and use of chlorofluorocarbons (CFCs) because of their adverse effect on the earth's ozone layer. A major use of chlorofluorocarbon R-12 was as a refrigerant in mobile air conditioning systems. Refrigerant R-134a was chosen by this industry as a non-ozone-depleting replacement for R-12.

In mobile A/C systems, the compressor lubricant travels through the system with the refrigerant. To ensure return to the compressor, the lubricant must have adequate solubility in the refrigerant. The mineral oils that are used as lubricants with R-12 are insoluble in R-134a. Polyalkylene glycol lubricants show good solubility in R-134a. Because of their good solubility and lubricating characteristics, PAG lubricants have been chosen by the automotive industry for use in R-134a A/C systems.

PAGs have a number of physical properties that enable them to perform well as refrigeration lubricants when used in conjunction with R-134a. These include their good solubility and stability in R-134a, excellent lubricity, and compatibility with many common elastomers. The good low temperature flow properties and low volatility of PAGs are also important in refrigeration applications.

While PAGs have a number of physical properties that are desirable in a refrigeration lubricant, it is their good solubility in R-134a that has led to their use in mobile A/C systems. PAG refrigeration lubricants exhibit excellent low temperature solubility. They also show a high temperature insolubility region at low PAG concentrations [61]. In general, the lower the viscosity of the PAG, the better the high temperature solubility.

In the high temperature insolubility region the R-134a/PAG mixture will separate into two layers. These two layers are not pure refrigerant and pure lubricant, but instead consist of a lubricant-rich phase and a refrigerant-rich phase. The composition of the two phases that form in the high temperature insolubility region can be determined from the intersection of the horizontal temperature tie line with the PAG's solubility curve [61].

The excellent low temperature miscibility of PAGs and R-134a, as well as their mutual solubility at elevated temperatures, ensures the circulation of lubricant through the A/C system that is necessary for good compressor lubrication.

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While lubricant solubility in the refrigerant is necessary, it is also important for the refrigerant/lubricant pair to be chemically and thermally stable. PAG lubricants exhibit excellent stability in R-134a. Sealed-tube stability tests run at 350°F (175°C) for 14 days in the presence of steel, aluminum, and copper coupons show the PAG/R-134a combination to be at least as stable as mineral oils run under the same conditions in the presence of R-12 [62,63].

PAGs are excellent lubricants. Of particular importance in refrigeration applications are the high viscosity indices of PAGs, typically ranging from 180 to over 250. PAG refrigeration lubricants thus show significantly less change in viscosity with temperature than do mineral oils, whose viscosity indices are typically less than 100. This means that compared to mineral oils, PAGs are more fluid at low evaporator temperatures and still provide good lubricity in the hot compressor.

PAGs are compatible with most common elastomers. However, it is important to consider the effect of the R-134a when both the refrigerant and lubricant are present. Because of the variations that can exist between elastomers in the same generic family, it is important to test the compatibility of the refrigerant/lubricant pair with the specific elastomers that are to be used in critical applications.

One of the major differences between PAGs and mineral oils is their affinity for water. PAGs are hygroscopic relative to mineral oil lubricants. PAG refrigeration lubricants usually have a maximum water specification of 1000 ppm and normally contain between 400 and 800 ppm water.

Because they are hygroscopic, PAGs will pick up water when exposed to humid air. They will continue to pick up water until an equilibrium or saturation level is achieved. Typical saturation levels range from 1 to 5%, depending on the humidity and the structure of the PAG.

It is important to realize that the water absorbed by PAGs is not free but is instead bound to the PAG backbone. Therefore neither corrosion nor ice crystal formation has been a problem in automotive A/C systems that are lubricated with PAGs.

Because of their hygroscopicity, PAG refrigeration lubricants should not be exposed to humid air during storage. Bulk storage tanks and drums should be nitrogen blanketed or equipped with vent dryers. For storage in small containers, minimizing air exposure is usually sufficient to keep PAG refrigeration lubricants in satisfactory condition.

There have been many questions asked regarding the proper handling of PAGs. PAG refrigeration lubricants are significantly less hygroscopic than brake fluids meeting U.S. Department of Transportation Standards (DOT-3). If the same care is taken when PAG lubricants are handled that is exercised in work with DOT-3 brake fluids, no performance problems should occur. Proper handling consists simply of keeping the lubricant container closed when not in use, and minimizing the amount of time the lubricant is exposed to the air during its transfer from the container to the A/C system. Any water that is introduced into an A/C system with the PAG will be removed by the molecular sieve dryer [64].

A challenge currently facing the automotive industry is how to service the R-12 vehicles on the road today as the supply of this refrigerant becomes scarce. Much work has been done in the automotive industry to determine the best ways to convert, or retrofit, these R-12 vehicles to R-134a. A retrofit lubricant must be compatible with residual R-12 and mineral oil as well as soluble in R-134a. Compressor makers, car manufacturers, and component suppliers have evaluated the use of PAGs as retrofit lubricants. PAGs have performed very well in these evaluations, and all major car companies have chosen PAG lubricants for use in the retrofitting of their vehicles.

One of the major requirements of a retrofit lubricant is stability in the presence of residual R-12. Analysis of the refrigerant in retrofit vehicles shows that the residual concentration of R-12 is typically about 1%. A worst-case retrofit would leave approximately 5% R-12 in the

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A/C system. Because of the ease with which the R-12 concentration can be reduced to low levels, concerns about contamination of the refrigerant supply, and the higher pressures exerted by R-12/R-134a mixtures [65], the Society of Automotive Engineers has declared that the concentration of R-12 must be reduced to below 2% [66].

High temperature and long-term sealed-tube tests show that PAG refrigeration lubricants are stable in the residual R-12 concentrations that can be expected in retrofit vehicles [61]. Also, the analysis of lubricant samples from retrofit tests on compressor stands and from actual retrofit vehicles has shown no signs of PAG or R-134a degradation.

PAGs are compatible with used mineral oils in that they do not undergo any adverse physical or chemical reactions when they are mixed. Some PAGs exhibit limited solubility in mineral oils, but their performance in retrofit applications is not adversely affected.

PAG lubricants have been used in retrofit trials where 50–100% of the original mineral oil charge was left in the A/C system. In most of these trials, no lubricant-related problems were experienced. The lubricant problems that did occur were due to lubricant slugging and subsequent compressor failure. Slugging is not caused by incompatibility between the PAG and mineral oil; rather, it is the result of too much lubricant in the system. Therefore, removing as much mineral oil as practical is generally recommended when a vehicle is being retrofitted from R-12 to R-134a.

Since PAG lubricants are compatible with residual R-12 and mineral oil, much work was done by the automotive industry to show that PAGs are good retrofit lubricants. Many different retrofit scenarios using R-134a and PAG lubricants were evaluated in an effort to determine the most cost-effective method for a given A/C system. In general, the performance of the PAG lubricants in these retrofit tests has been excellent. They provide good lubricity and have proven to be compatible with residual R-12 and mineral oil.

All major car manufacturers have decided to retrofit their vehicles with R-134a and PAG lubricants. To achieve a reliable, cost-efficient retrofit, however, different procedures are recommended for different vehicles. When retrofitting a vehicle from refrigerant R-12 to R-134a, it is important to follow the car maker's specific recommendations.

8. Two-Cycle Engine Lubricants

Polyalkylene glycols based on polypropylene glycol were recognized as lubricants for use with air cooled two-cycle engines as early as 1946 [11]. The excellent lubricating properties of polyalkylene glycol based two-cycle lubricants have been demonstrated over the years in competition Moto-cross and Enduro racing [67]. Freedom from plug fouling due to carbonaceous residues has been demonstrated repeatedly on test stands as well as in trail and street riding [68]. Polyalkylene glycol lubricants are also used as lubricants in high performance engine fuels for gocarts and model engines [69].

Polyalkylene glycols show good solubility in gasoline as well as methanol and nitromethane-methanol mixtures. They provide good lubricity and excellent detergency. The clean burn-off properties of polyalkylene glycol based two-cycle engine lubricants virtually eliminate engine problems related to spark plug fouling, combustion chamber deposits, and exhaust port plugging [36].

Recently Southwest Research performed Japanese Automobile Standards Organization (JASO) tests on a polyalkylene glycol two-cycle engine lubricant. The PAG-based product demonstrated excellent performance compared to a high quality petroleum oil based standard [67].

Four JASO tests were used to measure the following key two-cycle engine lubricant properties: lubricity and torque, detergency, smoke, and exhaust system blocking. In all four cases a high quality petroleum oil based product, JATRE 1, was used as a reference. A test result of 100 shows that the test lubricant performed as well as JATRE 1. A value of less than 100 means

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that the test lubricant did not perform as well as JATRE 1, while a value of greater than 100 indicates that the polyalkylene glycol lubricant outperformed the reference oil. These tests and the results of the work done to evaluate a polyalkylene glycol based two-cycle engine lubricant are summarized in Table 19.

JASO has three classifications of two-cycle engine lubricants. These categories are FA, FB, and FC, with FC being the most demanding. A Global Specification performance index has been proposed by the International Organization for Standardization (ISO). The ISO classifications are GB, GC, and GD, with GD representing the best rating. As can be seen in Table 19, polyalkylene glycol lubricants can be formulated to meet or exceed the requirements of the most demanding two-cycle engine lubricant classifications.

9. Crankcase Lubricants

The use of polyalkylene glycols as passenger car motor oils was pursued in the mid-1940s [11,70]. These synthetic lubricants, based on polypropylene glycol monobutyl ethers, were evaluated in engine test stands and in extensive vehicle trials. The very high viscosity indices and inherent good lubricity of these products resulted in wear of engine parts comparable to that of the best petroleum oils of the time. The polyalkylene glycol lubricants demonstrated a number of advantages relative to petroleum-based motor oils. These included less sludge formation, reduced combustion chamber deposits and spark plug fouling, excellent detergency, and better low temperature properties. However, distribution problems, poor compatibility with conventional petroleum oils, and high cost prevented polyalkylene glycol based automotive crankcase lubricants from being commercially successful.

Work is continually being done to improve the performance properties of engine lubricants. Higher viscosity indices are needed to provide good low temperature flow properties while retaining sufficient lubricity at the high temperatures that exist in today's engines. Good detergency reduces sludge formation. Better engine efficiencies, reduced emissions, and lower maintenance can be achieved by reducing the deposit-forming tendencies on intake valves and in the combustion chamber. These requirements have led to renewed interest in the use of polyalkylene glycols as engine crankcase lubricants because of their high viscosity indices, good detergency, and clean burn-off characteristics [71,72].

Oil-soluble polyalkylene glycols have recently been developed that solve the oil compatibility problems associated with conventional polyalkylene glycols while retaining the performance advantages provided by this class of synthetic lubricants. These new polyalkylene glycols are made from the copolymerization of propylene oxide and an α-olefin epoxide onto a lipophilic alcohol starter. Engine trials and other motor oil evaluation tests showed that multigrade syn-

Table 19 Results of JASO Testing of a Two-Cycle PAG Lubricant

		Official classifications				
JASO test	Property evaluated	JASO: FA ISO:	FB GB	FC GC	GC	Formulated PAG
M 340-92	Lubricity	90	95	95	105	111
M 340-99	Torque	98	98	98	98	99
M 341-92	Detergency	80	85	95	105	125
M 342-92	Smoke	40	45	85	85	85
M 343-92	Exhaust system blocking	30	45	90	90	300+[a]

[a] Test was stopped after it had run three times as long as the reference oil even though there was no sign of exhaust system blockage.

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thetic and semisynthetic lubricants containing these oil-soluble polyalkylene glycols provided the benefits expected from similar formulations containing esters and poly(α-olefins). In addition, the formulations containing the oil soluble polyalkylene glycols required less viscosity index improver and showed reduced volatility and improved engine cleanliness [72].

C. Market Size

Worldwide production of polyalkylene glycol for lubrication use is approximately 100 million pounds. The U.S. market represents about 50 million pounds. The polyalkylene markets for other uses, such as components in urethane foams or surfactants, dwarfs the use for products manufactured for lubrication purposes. In addition, the polyalkylene glycols manufactured for lubrication have other uses, such as heat transfer fluids, solder assist fluids, and metal quenchants, that are not included in the preceding estimates.

D. Environmental Information

1. Toxicology

Polyalkylene glycols enjoy a low degree of toxicity. As with any substance, Material Safety Data Sheets (MSDSs) should be consulted for any specific fluid. The toxicity of the base fluid can be effected by additives.

Toxicity by ingestion is low. The toxicity is highest for the lower molecular weight products. Measured LD_{50} values range from a low of about 4 mL/kg to over 60 mL/kg when rats were used as the test animal. Long-term feeding studies done on dogs and rats have shown minimal effects.

Toxicity by skin contact is low. Toxicity by absorption is generally very low. LD_{50} values by this route generally exceed 10 mL/kg. Skin sensitization is a function of molecular weight, with the lower molecular weight fluids showing the greatest effect. In general, the effects, if any, are a transient redness of the skin.

Because of the low vapor pressure of polyalkylene glycols toxicity by inhalation is generally very low. For the higher molecular weight copolymers of ethylene oxide propylene oxide that are monobutyl ethers, however, mechanically generated mists were found to be toxic upon inhalation. The products of thermal degradation, like those of any organic product, are toxic. Mechanical ventilation should be reviewed where mists or thermal degradation products are likely to be present. Eye injury is expected only for the lowest molecular weight polyalkylene glycols. The lower molecular weight fluids cause slight to moderate eye injury.

2. FDA Status

Because of their low degree of toxicity, polyalkylene glycols have been approved for a variety of uses where they might come into contact with food. These include the use in lubricants that are used to manufacture and otherwise process food (21 CFR 178.3570) and in a variety of foam control applications.

3. Environmental Effects

Users of lubricants should always be concerned with the effects to the environment, should the lubricant be spilled. Many claims are made as to biodegradability without considering the toxicity of the lubricant to other species. The environmental effects of polyalkylene glycols [73] are summarized in Table 20.

Polyalkylene glycols are biodegradable, but the speed of degradation depends on molecular weight. The lower molecular weight polyalkylene glycols biodegrade very readily. The higher

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Table 20 Environmental Effects of Polyalkylene Glycols

Type of molecule	Oxide	Molecular weight	Sturm biodegradation (% biodegradation in 28 days)	Concentrations (mg/L) 96-hour fathead minnow acute toxicity, LC_{50}[a]	48-hour *Daphnia magna* acute toxicity, EC_{50}[a]	Bacterial inhibition IC_{50}[a]
Monobutyl ether	100% PO	340	84	190	450	2,800
		740	99	86	250	1,300
		1,020	85	37	69	34,000
		1,550	48	20	26	19,000
		2,490	23	180	520	>50,000
Monobutyl ether	50:50 EO/PO	520	93	3,200	4,300	18,500
		970	65	13,000	5,400	40,000
		1,700	45	24,500	21,000	32,000
		3,930	7	11,900	17,000	10,000
Diol	75:25[b] EO/PO	2,470	71	129,000	88,000	38,000
		12,000	8	65,000	83,000	94,000
Water/glycol thydraulic fluid concentrate			57	6,700	1,400	36,000
Water/glycol hydraulic fluid			64	4,500	4,800	22,000

[a] LC_{50} = median lethal concentration (expected 50% mortality), EC_{50} = median effect concentration (expected 50% loss of mobility); IC_{50} = median inhibition concentration (expected 50% loss of respiration).

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molecular weight fluids biodegrade, but the biodegradation is slow, probably because transport across bacterial membranes is slow for large molecules.

In theory, it is possible to design a biodgradation composter by choosing the appropriate bacteria. The bacteria used in the tests described in Table 20 were extracted from a municipal wastewater treatment facility. Bacteria can be chosen that will degrade polyethylene glycols of all molecular weights. A combination of *Flavobacterium* sp. and *Pseudomonas* sp. will result in the degradation of 99% of polyethylene glycol of 6000 molecular weight in 7 days [74]. Each of these bacterial species utilizes the other's metabolism products.

One technique that will increase the speed of biodegradation of polyalkylene glycols is to treat the waste stream with ozone [75,76]. This has the effect of breaking the chain into smaller pieces, more easily utilized by the bacteria.

The effect of polyalkylene glycols on aquatic animals is low. Table 20 shows the effects on fathead minnows and on *Daphnia magna.* The largest effects are with the water-insoluble polypropylene glycol monobutyl ethers. The water-soluble products can have effects that are very low, with negligible effects on the environment expected. This advantage is important when combined with biodegradation rate. A slowly biodegraded polymer that has very low toxicity presents a very low risk to the environment.

Polyalkylene glycols present a very low risk to bacteria, as shown in Table 20. This is important in wastewater treatment facilities. If the effect on bacteria is low, there is little risk of poisoning the microorganisms in the facility.

Although polyalkylene base fluids have properties associated with environmental friendliness, additives can make substantial differences in human and environmental toxicity. The MSDS should contain this information.

The environmental fate of one type of formulated polyalkylene glycol, the water/glycol hydraulic fluids, is also shown in Table 20. The water/glycol fluids in Table 20 are based on diethylene glycol.

VI. OUTLOOK

Polyalkylene glycols are unique among lubricants. They can have almost any solubility characteristics, and they are the only water-soluble class of lubricants. In addition, their cleanliness, especially their low tendency to form carbon deposits, is extremely important.

Polyalkylene glycols will continue to enjoy modest growth, unless a large market develops (e.g., in automotive engine lubricants). The growth in chemical modification of existing structures is expected to continue.

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